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# Simulations of Fluorescence Solvatochromism in Substituted PPV Oligomers from Excited State Molecular Dynamics with Implicit Solvent

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**Abstract**

An efficient method of treating solvent effects in excited state molecular dynamics (ESMD) is implemented and tested by exploring the solvatochromic effects in substituted *p*-phenylene vinylene oligomers. A continuum solvent model is used which has very little computational overhead. This allows simulations of ESMD with solvent effects on the scale of hundreds of picoseconds for systems of up to hundreds of atoms. At these time scales, solvatochromic shifts in fluoresence spectra can be described. Solvatochromic shifts in absorption and fluorescence spectra from ESMD are compared with time-dependent density functional theory calculations and experiments.

*Keywords:* implicit solvent, excited state, molecular dynamics, solvatochromism, PPV, absorption, fluorescence, solvent, linear response

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## 1. Introduction

The excited state (ES) dynamics of molecular chromophores can be affected by a solvent or other environment as is evident in the phenomenon of solvatochromism. Solvatochromism is a shift in the energy of absorption or emission due to solvation. This is most often caused by electrostatic effects, but can also be due to aggregation, hydrogen bonding, or chemical reactivity.[1, 2, 3] Harnessing solvatochromism is useful for a huge number of technological and practical applications,[4, 5, 6] as well as fundamentally interesting for the study of molecular optical properties.[7, 8, 9] Simulations of solvatochromism are useful for understanding its molecular origin and for the design of new materials.[10, 11, 12] To date, few studies have explored the solvatochromic effects using excited state molecular dynamics (ESMD) due to the computational cost of increasing the system size. In this letter, we use implicit solvent models in ESMD to treat solvent effects at little additional computational cost compared to ESMD in vacuum.

In ESMD, each time step requires a quantum chemical calculation of the ES electronic structure. For a solute-solvent system, one could perform a fully quantum mechanical atomistic simulation of both solute and solvent. For realistic systems, this rapidly becomes prohibitively expensive as the system size grows. ESMD with solvent can be made feasible by treating the solvent in an approximate way. The most popular approximate atomistic treatment for ab initio molecular dynamics of the ground state (GS) is a combined quantum-mechanics/molecular mechanics (QM/MM) approach.[13, 14, 15] This requires averaging over many solvent configurations. Further, to accurately sample the excited state potential energy surface using ESMD, multiple ES trajectories starting from different GS configurations are required. This simulates a photoexcited wavepacket of nuclear configurations. Combined with various solvent configurations, the number of simulations becomes too large for solute/solvent systems using QM/MM in ESMD because for each solute configuration, multiple solvent configurations must be considered. On the other hand, implicit solvent models effectively average over all possible solvent configurations by treating the solvent as a continuum. Viscous and thermal effects can be treated with a Langevin equation of motion while electrostatic effects, the main source of solvatochromism, are efficiently simulated with a dielectric continuum model.

Two popular implicit solvent models, the polarizable continuum model (PCM) and conductor-like PCM (CPCM), simulate the solvent dielectric ef-

fects by modeling the solute as a system embedded in a dielectric cavity.[16] The cavity is assumed to have a distribution of induced surface charge which is determined from the solute charge density by solving Poisson's equation. This induced cavity surface charge effectively screens the Coulomb interactions in the solute Hamiltonian. Thanks to the availability of analytical gradients in time-dependent density functional theory (TD-DFT) and time-dependent Hartree-Fock (TD-HF) type calculations when the solvent is treated in a linear response (LR) formalism, it is possible to include implicit solvent effects in the ES at very little additional cost.[17] In this model, the dielectric screening effect of the solvent is included in calculations of the first-order optical response. The solvent responds linearly to the excitation of the solute.[18] In more specific terms, the solvent becomes polarized by the transition density calculated from TD-HF or TD-DFT calculations. This is in contrast to state-specific (SS) type models, where the solvent is polarized by the excited state charge density of the solute.[19, 20, 21, 18]. The LR formalism is used in this work to describe solvent effects in ESMD calculations. Further, single-point calculations of LR and SS models are compared.

Oligo(*para*-phenylene vinylene) (PPVO) derivatives are investigated to explore the simulation methods. The chemical structure of these molecules are shown in Figure 1.[22, 23] This class of conjugated materials is rapidly evolving in applications such as molecular electronics and nanotechnology or as photovoltaic and electrochromic devices.[24, 25, 26] The specific molecules studied here have been implicated as excellent candidates for light-emitting diodes, showing varied emission energies ranging accross the optical spectrum.[25, 26]

The goal of this letter is to describe the inclusion of LR polarizable continuum solvent in ESMD and compare the solvatochromic effects simulated in this way with other methods. To date, ESMD with implicit solvent effects has so far only been performed by including an Onsager model in the GS self-consistent field methods.[27] This neglects both molecular shape and screening of the excitations. The simulations performed here are intended to be extended by including LR and SS type solvent models in non-adabatic ESMD in later publications.

## 2. Excited State Molecular Dynamics Simulations

Born-Oppenheimer molecular dynamics on the GS or ES molecular PES are performed here. The evolution of a molecule before and after photoexci-

tation is followed using the previously developed ESMD approach to calculate classical nuclear trajectories on the excited-state adiabatic PES.[28, 29, 30, 31] For calculations of the ES density matrix, we use the semiempirical AM1 method in a TD-HF scheme (referred to as TD-AM1).[28] The AM1 method, along with other semiempirical methods such as PM3, are not as accurate as well tuned density functional theory (DFT) calculations of properties such as heat of formation and geometric structure, but have a significantly reduced computational cost and very reasonable accuracy.[32, 33] Similarly, TD-AM1 calculations have significantly less computational cost but with reduced accuracy in comparison to TD-DFT .[34, 35] In comparison to experimental optical spectra, TD-AM1 performs quite well for conjugated organic molecules such as those studied in this work.[36, 37, 34]

This method is coupled with the conductor-like polarizable continuum model (CPCM) using a standard tesselation scheme for cavity surface discretization. [38, 39] The strength of the solvent dielectric effect is given by a coefficient calculated from the dielectric constant, $\epsilon$, where the coefficient is[38, 39]

$$f(\epsilon) = \frac{\epsilon - 1}{\epsilon}. \tag{1}$$

By choosing $\epsilon = 5$, which gives $f(\epsilon) = 0.8$, the simulations of solvent effects are applicable to a broad family of organic solvents, ranging from non-polar to low polarity.

The solvent effects simulated here are considered to be *equilibrium* solvation. This is a result of an assumption that the solvent is always in equilibrium with the solute. Since solvent reorganization occurs on multiple time scales, improvement of the model used here will require nonequilibrium solvation effects.[20] This will involve treatment of nonequilibrium effects associated with both electronic transitions and molecular motion. It is important to note that the calculations of electronic transitions performed here are strictly vertical, since no solvent reorganization is assumed to occur during the electronic transitions. In formulations designed for single-point calculations, a partition of the effective solvent potential is assumed to follow the electronic transition exactly.[40, 20] This will become more complicated in ESMD, since the time-dependence of solvent effects from a frequency dependent dielectric constant will be important.[41, 42] These effects are neglected in all ESMD and TD-DFT simulations explored in this letter.

For all simulations, molecules were propagated on the ground or lowest energy ES PES according to the Langevin equation of motion[43] at room

temperature (300 K) using a time step of 0.5 fs and a friction coefficient of 2.0 $ps^{-1}$. To simulate the absorption spectrum, each molecule was propagated on the GS PES to prepare an initial trajectory of 200 ps. From this trajectory, 20 snapshots were taken at 10 ps intervals to give initial positions and velocities. Each snapshot was propagated similarly for 100 ps. The calculated $S_1$ excitation energies ($\Omega$) at each time step were then histogram binned with weighting by the calculated oscillator strengths and normalized to simulate the normalized absorption spectra of the molecules.

To simulate the fluorescence spectrum, a set of initial positions and velocities for propagation on the first singlet ES PES were prepared by propagating a single trajectory on the GS PES as described above. Then, 100 snapshots were collected from the GS trajectory at 2 ps intervals. These initial conditions were used as starting points for propagation on the ES PES to simulate photoexcitation. The ensemble of initial trajectories were then propagated on the first singlet ES PES for 200ps. The $\Omega$ at each time step were histogram binned in the same way as described above, giving normalized fluorescence spectra.

Single point calculations of the molecular absorption and fluorescence using TD-DFT were also performed with the CAM-B3LYP functional and 6-31G* basis set (referred to as TD-CAM-B3LYP). Two ES solvation models were tested, LR[17] and state specific (SS).[19] CPCM with $\epsilon = 5$ was used for comparison with ESMD results. Absorption energies were determined from the optimized GS geometries in vacuum. Fluorescence energies were determined from the optimized ES geometries in vacuum. The difference in vertical excitation energy between vacuum and solvent calculations is taken as the solvatochromic shift. These simulations were performed with the Gaussian 09 program.[44]

## 3. Results and Discussion

To visualize the solvatochromic effects, we subtract the mean energy of the absorption or fluorescence spectra simulated in vacuum from the spectral simulations in solvent. This is called the solvatochromic shift and is denoted by $\Delta\Omega$. Figure 2 shows the solvatochromic shifts in the absorption spectra while Figure 3 shows the solvatochromic shifts in the fluorescence spectra. All solvatochromic shifts calculated with ESMD are bathochromic, i.e. red shifted.

The mean solvatochromic shift predicted in this way is nearly two times larger in the fluorescence spectra than in the absorption spectra. In general, the magnitude of either the absorption or fluorescence solvatochromic shifts only vary by a small amount (approximately 0.01 eV) when the substituent is changed. These shifts correspond quite well to single-point calculations using the same method (TD-AM1). The magnitude and ordering of the absorption solvatochromic shifts with substituent is nearly the same. The fluorescence solvatochromism predicted by single point calculations has little variation amongst various substitutents as is also observed in ESMD simulations. Interestingly, the mean fluorescence solvatochromic shifts are significantly larger than the single point calculations by approximately 0.3 eV. This is explained by the photoexcited wavepacket and thermal motion of the molecule during the excited state lifetime simulated in ESMD. The minimum energy conformation may have a smaller solvatochromic shift than what is observed in photoemission since the molecule emits from various configurations which may have stronger solvatochromic effects.

Next, we compare single point calculations from TD-AM1 calculations with TD-CAM-B3LYP and experiment. When compared to experimental results, absolute transition energies calculated with TD-CAM-B3LYP are blue shifted, while those calculated with TD-AM1 are red shifted.[25] These absolute excitation energies are given in the supporting information. The relative shifts due to solvent provide a more favorable comparison than absolute energies. From Table 1, TD-CAM-B3LYP calculations tend to predict larger solvatochromic shifts than TD-AM1. The ratio of solvatochromic shifts between TD-AM1 and TD-CAM-B3LYP in either the absorption or fluorescence are similar for all molecules.

Direct comparison with experiment is difficult due to aggregation effects.[25, 26] Aggregation effects cause excimer emission which is strongly red or blue shifted depending on the substituent and are not captured by ESMD of single molecules.[25, 26] No data exists yet exists for solvatochromic shifts in these molecules which is completely free of aggregation effects. Nonetheless, experiments from Refs. [25] and [26] performed with varied solvents suggest that the the solvatochromic shifts without aggregation effects are larger in fluorescence than in absorption, approximately 0.2 eV and 0.05-0.1 eV, respectively. These observations are in general agreement with the simulations and the predicted shifts are of reasonable magnitude for conjugated organic molecules.[1, 26]

Comparison of linear response and state-specific solvent models in Table 1

is reflective of greater charge-transfer character of the excited states predicted by TD-CAM-B3LYP relative to TD-AM1. This point is confirmed by the difference in dipole moment between the ground and excited states given in the supporting information. A large difference in dipole moment between the ground and excited state describes charge-transfer character. Simulated solvation by the SS model involves this difference in dipole moment, but does not involve the transition dipole. On the other hand, the LR model involves the transition dipole but not the difference in dipole moment.[18] The solvatochromic shifts predicted by TD-AM1 using the SS model are smaller than with LR model due to relatively little predicted charge-transfer character. For molecules with the largest dipole moments, i.e. $\mathbf{R}_1 = NO_2$, TD-CAM-B3LYP predicts rather large solvatochromic shifts for simulations with the SS model since the CAM-B3LYP functional predicts significant charge-transfer character.

An alternative approach to that given in Ref. [20] for the calculation of fluorescence energies in solution with the SS model is used here. In Ref. [20], a nonequilibrium solvation calculation of the GS energy is performed and subtracted from the equilibrium solvated ES energy.[40] This corresponds to some instantaneous partial reorganization of the solvent upon photon emission. In the approach taken here for comparison to the fluorescence energies calculated with the LR model in ESMD, we assume that no solvent reorganization takes place instaneously. This approximation may be better suited to describe the ES PES energy from TD-DFT calculations with the SS model than fluorescence energies. It is suitable for comparison with results from the LR model, since the LR model does not involve equilibration with solvent charges derived from the ES charge density[18]

Simulations of solvent effects in ESMD are not designed to reproduce experimental optical spectra with high accuracy, but to include solvent effects in the relative energetics predicted in ESMD with little overhead in terms of required CPU hours per computation. This is achieved with an average increase of approximately 15% (actual simulation times given in supporting formation). In a correct reproduction of optical spectra, the optical dielectric constant would be used for calculations of the excitation energy since it describes an instantaneous transition. This is generally smaller than the static dielectric constant, so our results are expected to overemphasize the solvatochromic shifts compared to experiment.

The molecules studied here are donor-acceptor type molecules and may thus display some intramolecular charge-transfer character in excited states[25].

Solvation of such excitations can be more accurately described by the SS model.[18] Further work will explore dynamics with SS effects using recently formulated analytical gradients for a similar model.[45] Non-adiabatic ESMD with solvent effects will also be explored.

## 4. Conclusion

This letter describes ESMD simulations which include solvent effects at little additional computational cost. Low cost is achieved by an implementation of the LR solvent formalism with the CPCM continuum solvent potential. This allows inclusion of the dielectric effects of the solvent in dynamic simulations on the scale of hundreds of picoseconds for molecules of up to hundreds of atoms. Our analysis included comparisons with single point calculations from TD-AM1 and TD-CAM-B3LYP methods with both the LR and SS solvent models. ESMD simulations including SS effects, as well as solvent effects in non-adiabatic ESMD will be described in the future.

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Table 1: Shifts in excitation energies calculated with from single point calculations using TD-AM1 and, in parentheses, TD-CAM-B3LYP. Values are given in eV. Geometries for calculations are optimized in vacuum. Equilibrium solvation with $\epsilon = 5$ is used for LR and SS solvent calculations.

| | | Absorption | | Fluorescence | |
|---|---|---|---|---|---|
| $\mathbf{R}_1$ | $\mathbf{R}_2$ | LR | SS | LR | SS |
| $H$ | $H$ | -0.081(-0.114) | -0.011(-0.011) | -0.102(-0.156) | -0.006(-0.006) |
| $CO_2H$ | $H$ | -0.078(-0.121) | -0.011(-0.045) | -0.100(-0.163) | -0.010(-0.028) |
| $NH_2$ | $H$ | -0.087(-0.121) | -0.017(-0.022) | -0.111(-0.165) | -0.021(-0.019) |
| $NO_2$ | $H$ | -0.078(-0.146) | -0.020(-0.182) | -0.101(-0.184) | -0.027(-0.112) |
| $NO_2$ | $NH_2$ | -0.082(-0.150) | -0.019(-0.251) | -0.110(-0.203) | -0.033(-0.156) |

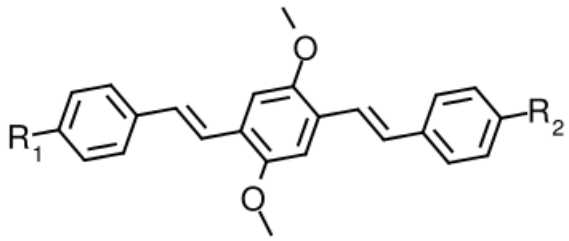


Figure 1: Structure of substitued PPV oligomer molecules. $\mathbf{R}_1 = H, NO_2, NH_2, CO_2H$ with $\mathbf{R}_2 = H$ and $\mathbf{R}_1 = NO_2$ $\mathbf{R}_2 = NH_2$

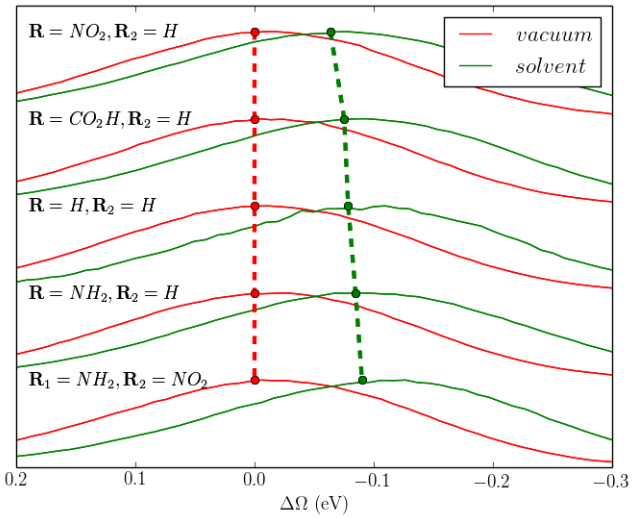


Figure 2: Magnitude of simulated solvatochromic shift ($\Delta\Omega$) in the absorption spectra of substituted PPV oligomers. Dotted lines connect the mean energies for each peak.

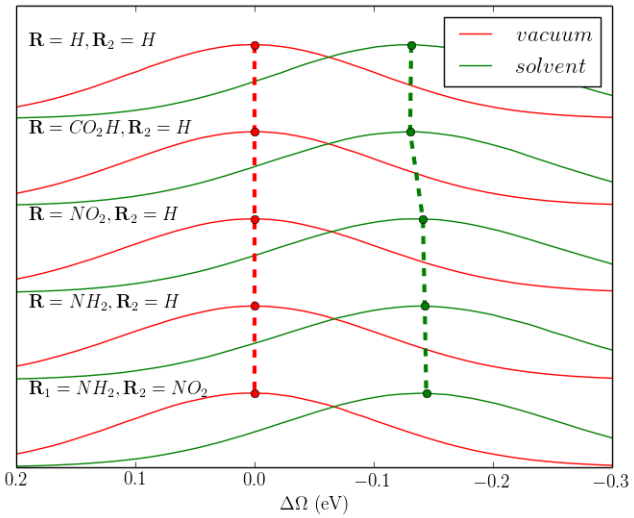


Figure 3: Magnitude of simulated solvatochromic shift ($\Delta\Omega$) in the fluorescence spectra of substituted PPV oligomers. Dotted lines connect the mean energies for each peak.